Chapter 14. Industrial Ecology

by
David T. Allen

The environmental performance of chemical processes is governed not only by the design of the process, but also by how the process integrates with other processes and material flows. Consider a classic example - the manufacture of vinyl chloride.

Billions of pounds of vinyl chloride are produced annually. Approximately half of this production occurs through the direct chlorination of ethylene. Ethylene reacts with molecular chlorine to produce ethylene dichloride (EDC). The EDC is then pyrolyzed, producing vinyl chloride and hydrochloric acid.

$$Cl_2 + H_2C{=}CH_2 \Rightarrow Cl\,H_2C\text{-}CH_2\,Cl$$

$$Cl\,H_2C\text{-}CH_2\,Cl \Rightarrow H_2C{=}CH\,Cl + HCl$$

In this synthesis route, one mole of hydrochloric acid is produced for every mole of vinyl chloride. Considered in isolation, this process might be considered wasteful. Half of the original chlorine winds up, not in the desired product, but in a waste acid. But the process is not operated in isolation. The waste hydrochloric acid from the direct chlorination of ethylene can be used as a raw material in the oxychlorination of ethylene. In this process, hydrochloric acid, ethylene and oxygen are used to manufacture vinyl chloride.

$$HCl + H_2C{=}CH_2 + 0.5\ O_2 \Rightarrow H_2C{=}CH\,Cl + H_2O$$

By operating both the oxychlorination pathway and the direct chlorination pathway, as shown in Figure 14.1-1, the waste hydrochloric acid can be used as a raw material and essentially all of the molecular chlorine originally reacted with ethylene is incorporated into vinyl chloride. The two processes operate synergistically and an efficient design for the manufacture of vinyl chloride involves both processes.

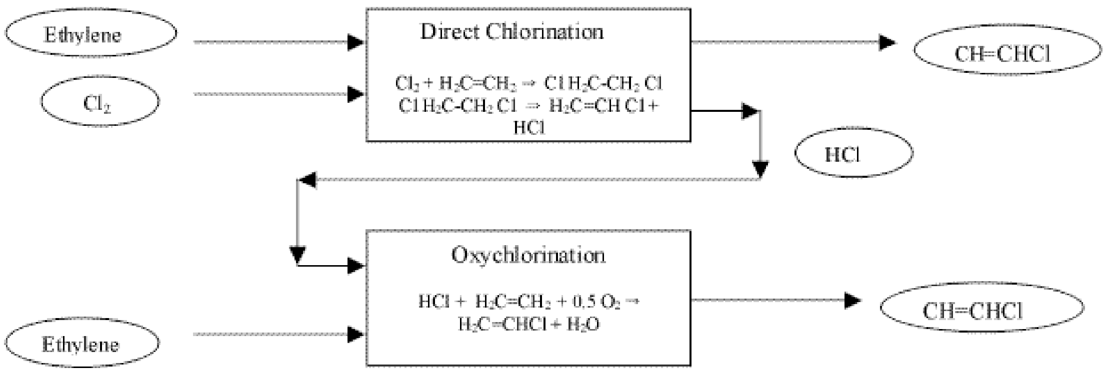


Figure 14.1-1 Byproduct hydrochloric acid from the direct chlorination of ethylene is used as a raw material in the oxychlorination process; by operating the two processes in tandem, chlorine is used efficiently.

Additional efficiencies in the use of chlorine can be obtained by expanding the number of processes included in the network. In the network involving direct chlorination and oxychlorination processes, both processes incorporate chlorine into the final product. Recently, more extensive chlorine networks have emerged linking several isocyanate producers into vinyl chloride manufacturing networks (McCoy, 1998). In isocyanate manufacturing, chlorine is reacted with carbon monoxide to produce phosgene:

$$CO + Cl_2 \qquad COCl_2$$

The phosgene is then reacted with an amine to produce an isocyanate and byproduct hydrochloric acid:

$$RNH_2 + COCl_2 \qquad RNCO + 2\ HCl$$

The isocyanate is subsequently used in urethane production, and the hydrochloric acid is recycled. The key feature of the isocyanate process chemistry is that chlorine does not appear in the final product. Thus, chlorine can be processed through the system without being consumed. It may be transformed from molecular chlorine to hydrochloric acid, but the chlorine is still available for incorporation into final products, such as vinyl chloride, that contain chlorine. A chlorine-hydrogen chloride network incorporating both isocyanate and vinyl chloride has developed in the Gulf Coast of the United States. The network is shown in Figure 14.1-2. Molecular chlorine is manufactured by Pioneer and Vulcan Mitsui. The molecular chlorine is sent to both direct chlorination processes and to isocyanate manufacturing. The byproduct hydrochloric acid is sent to oxychlorination processes or calcium chloride manufacturing. The network has redundancy in chlorine flows, such that most processes could rely on either molecular chlorine or hydrogen chloride.

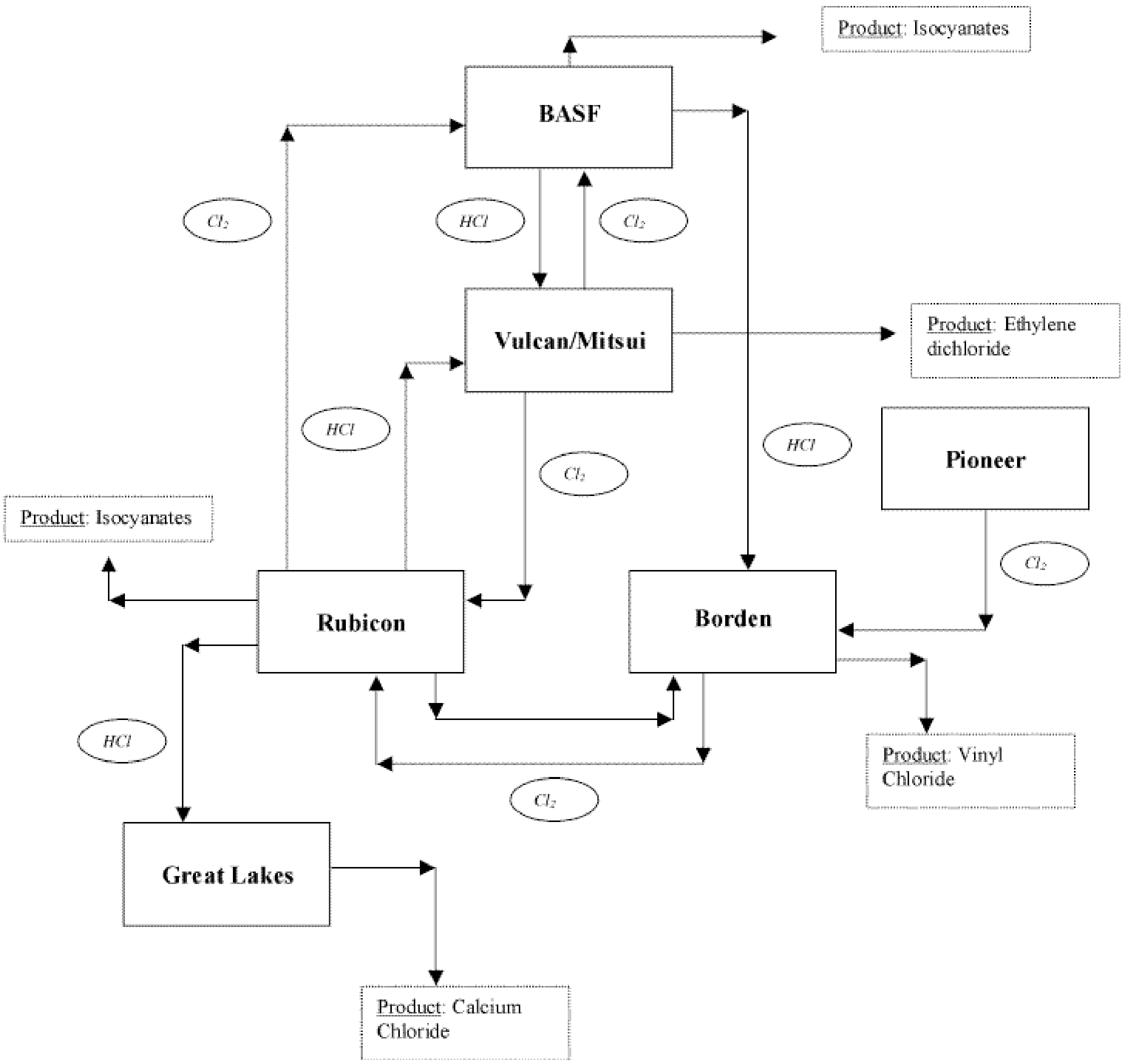


Figure 14.1-2 Chlorine flows in combined vinyl chloride and isocyanate manufacturing.

Consider the advantages of this network to the various companies (Francis, 2000).

- Vulcan/Mitsui effectively rents chlorine to BASF and Rubicon for their isocyanate manufacturing; the chlorine is then returned in the form of hydrochloric acid for ethylene dichloride/vinyl chloride manufacturing

- BASF and Rubicon have guaranteed supplies of chlorine and guaranteed markets for their byproduct HCl.

Even more complex networks could, in principle be constructed. As shown in Table 14.1-1, chlorine is used in manufacturing a number of non-chlorinated products. Table 14.1-1 lists, for selected reaction pathways, the pounds of chlorinated intermediates used along the supply chain, per pound of finished product. This ranking provides one indication of the potential for networking these processes with processes for manufacturing chlorinated products (see Rudd, et al., or Chang, 1996).

Table 14.1-1 Partial Listing of Non-Chlorinated Chemical Products That Utilize Chlorine in their Manufacturing Processes (Chang, 1996).

Product	Synthesis Pathway	Pounds of chlorinated intermediates per pound of product
Gylcerine	Hydrolysis of epichlorohydrin	4.3
Epoxy Resin	Epichlorohydrin via chlorohydrination of allyl chloride, followed by reaction of epichlorohydrin with bisphenol-A	2.3
Toluene diisocyanate	Phosgene reaction with toluenediamine	2.2
Aniline	Chlorobenzene via chlorination of benzene, followed by reaction of chlorobenzene with ammonia	2.2
Phenol	Chlorobenzene via chlorination of benzene, followed by dehydrochorination of chlorobenzene	2.1
Methylene diphenylene diisocyanate	Phosgene reaction with aniline (also produced with chlorinated intermediates)	1.5
Propylene oxide	Chlorination of propylene	1.46

An examination of individual processes, such as those listed in Table 14.1-1, can be useful in building process networks, but the individual process data do not reveal whether efficient use of chlorine is a major or a minor issue in chemical manufacturing. To determine the overall importance of these flows, it is useful to consider an overall chlorine balance for the chemical industry. The overall flows of chlorine into products and wastes, as well as the recycling of chlorine in the chemical manufacturing sector, is shown in Figure 14.1-3. The data indicate that roughly a third of the total chlorine, eventually winds up in wastes. By employing the types of networks shown in Figures 14.1-1 and 14.1-2, the total consumption of chlorine could be reduced.

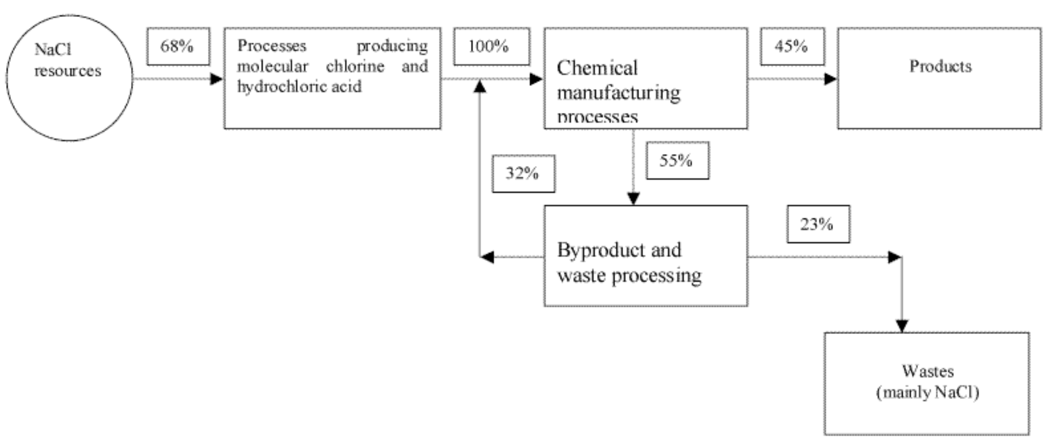


Figure 14.1-3 A summary of flows of chlorine in the European chemical manufacturing industry (Francis, 2000).

Identifying which processes could be most efficiently integrated is not simple and the design of the ideal network depends on available markets, what suppliers and markets for materials are nearby, and other factors. What is clear, however, is that the chemical process designers must understand not only their process, but also processes that could supply materials, and processes that could use their byproducts. And, the analysis should not be limited to chemical manufacturing. Continuing with our example of waste hydrochloric acid and the manufacture of vinyl chloride, by-product hydrochloric acid could be used in steel making or by-product hydrochloric acid from semiconductor manufacturing might be used in manufacturing chemicals.

Finding productive uses for byproducts is a principle that has been used for decades in chemical manufacturing. What is relatively new, however, is the search for chemical byproduct uses in industries that extend far beyond chemical manufacturing. This chapter will examine both of these topics - the overall flows of raw materials, products and by-products in chemical manufacturing industries – as well as the potential for combining material and energy flows in chemical manufacturing with material and energy flows in other industrial sectors. Variously called by-product synergy, zero waste systems, or even industrial ecology, the goal of this design activity is to create industrial systems that are as mass efficient as possible.

Section 14.2 provides an overview of material flows in chemical manufacturing and describes analysis methods that can be used to optimize flows of materials. Section 14.3 examines case studies of exchanges of materials and energy across industrial sectors and the emerging concept of eco-industrial parks. Finally, section 14.4 briefly attempts to assess the potential benefits of by-product synergies.

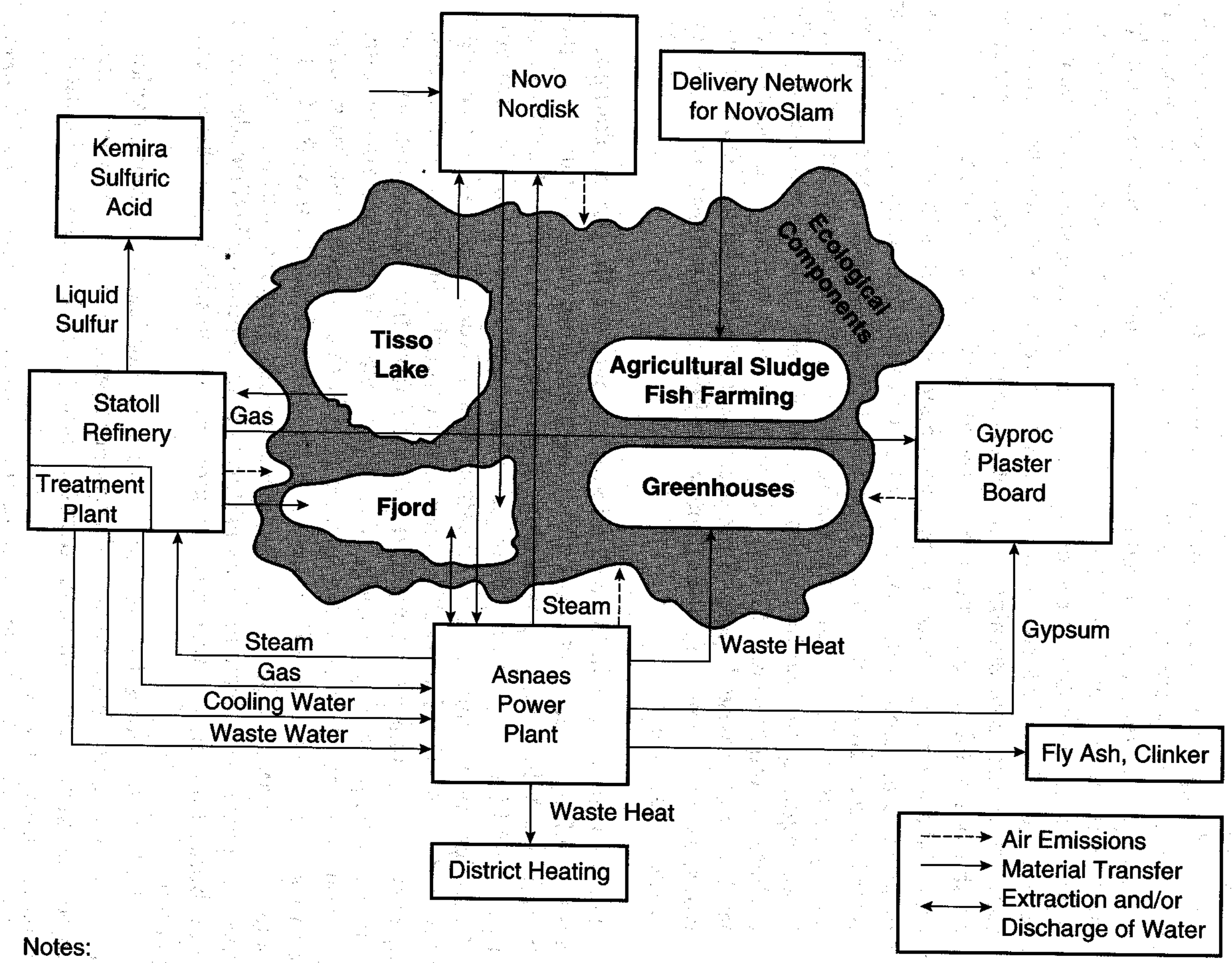
Box 1 What is Industrial Ecology?

The phrase “Industrial Ecology” evokes powerful images and strong reactions, both positive and negative. To some, the phrase conjures images of industrial systems that mimic the mass conservation properties of natural ecosystems. Powerful analogies can be drawn between the evolution of natural ecosystems and the potential evolution of industrial systems. Billions of years ago, the Earth’s life forms consumed the planet’s stocks of materials and changed the composition of the atmosphere. Our natural ecosystems evolved slowly to the intricately balanced, mass conserving networks that exist today. Can our industrial systems evolve in the same way, but much more quickly? These are interesting visions and thought provoking concepts. But, is Industrial Ecology merely a metaphor for these concepts? Is there any engineering substance to the emerging field of Industrial Ecology?

As demonstrated in this chapter, Industrial Ecology is much more than a metaphor and it is a field where engineers can make significant contributions. At the heart of Industrial Ecology is the knowledge of how to reuse or chemically modify and recycle wastes – making wastes into raw materials. Chemical engineers have practiced this art for decades. The history of the chemical manufacturing industries provides numerous examples of waste streams finding productive uses. Nonetheless, even though the chemical manufacturing industries now provide excellent case studies of Industrial Ecology in practice – networked and mass efficient processes – there is much left to be done. While the chemical manufacturing industries are internally integrated, is relatively little integration between chemical manufacturing and other industrial sectors and between chemical manufacturers and their customers.

Engineers could take on design tasks such as managing the heat integration between a power plant and an oil refinery or integrating water use between semiconductor and commodity material manufacturing. The goal is to create even more intricately networked and efficient industrial processes – an industrial ecology. Not all of the tools needed to accomplish these goals are available yet, but this Chapter begins to describe the basic concepts and suggests the types of tools that the next generation of process engineers will require.

Chapter 14 Example Figure



Notes:
(1) This figure is not drawn to scale, nor is it an accurate geographic depiction.
(2) Unused residuals resulting from all activities in the industrial ecopark are eventually released into the biosphere.

Figure 14.3-1 The industrial network at Kalundborg, Denmark. (Ehrenfeld and Gertler, 1997)

Chapter 14 Sample Homework Problem

At the Kalundborg ecopark, waste heat in the form of steam is sent from the AsnFs Power Stattion to the Statoil refinery (140,000 tons/year), to the Novo Nordisk pharmaceutical manufacturing facility (215,000 tons/year), and to district heating (225,000 tons/year). The power plant is rated at 1,500 megawatts, and the steam has a recoverable heat of 1,000 BTU/lb. Each year the power plant burns approximately 4.5 million tons of coal rated at 10,000 BTU/lb.

a) Calculate the fraction of the energy from coal combustion that goes to electricity generation, to the refinery, to the pharmaceutical plant, and to district heating. What is the total rate of energy utilization?

b) Not all of these energy demands will operate on similar cycles. Project the daily and seasonal variations in demand and suggest ways for the power plant to meet these needs.

Calculate the quantity of residential heating oil consumption that is displaced by the use of steam. If oil costs $2.00 per gallon and each gallon has a heating value of approximately 5*105 BTU, what is the value of this resource?